THE CLAIMS

What is claimed is:

1. A deposition composition for depositing material on a substrate, said deposition composition comprising a supercritical fluid and a precursor of the material to be deposited on the substrate.

2. The deposition composition of claim 1, wherein the supercritical fluid comprises a fluid selected from the group consisting of: carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, ethane, methanol, ethanol, isopropanol, dimethyl ketone, sulfur hexafluoride, carbon monoxide, dinitrogen oxide, forming gas, hydrogen, and mixtures thereof.

3. The deposition composition of claim 1, wherein the supercritical fluid comprises carbon dioxide.

4. The deposition composition of claim 1, wherein said composition comprises a co-solvent.

5. The deposition composition of claim 1, consisting essentially of said supercritical fluid and said precursor.

6. The deposition composition of claim 1, consisting of said supercritical fluid and said precursor.

7. The deposition composition of claim 1, wherein said precursor comprises a barrier layer precursor for forming a metal nitride or metal oxynitride barrier layer.

8. The deposition composition of claim 7, wherein said metal nitride or metal oxynitride comprises at least one metal selected from the group consisting of tantalum, titanium, silicon, tungsten and molybdenum.

9. The deposition composition of claim 1, wherein said precursor comprises a precursor for forming a mesoporous organo-functionalized silsequioxane (SSQ) material on the substrate.

10. The deposition composition of claim 1, wherein said precursor comprises a precursor for forming a low k organosilicate material on the substrate.

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11. The deposition composition of claim 10, wherein the precursor comprises a silsequioxane or siloxane precursor.

12. The deposition composition of claim 11, wherein the precursor comprises a silsequioxane.
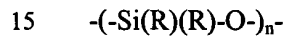
13. The deposition composition of claim 12, wherein the silsequioxane has the formula:
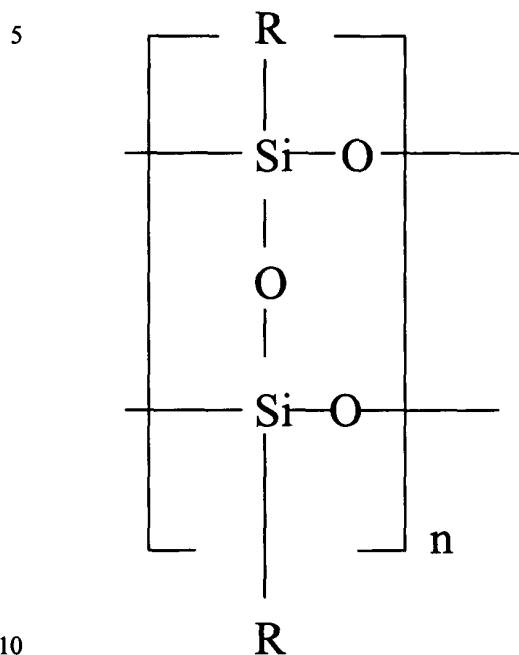
$$
\left[
\begin{array}{c}
R \\
| \\
Si{-}O \\
| \\
O \\
| \\
Si{-}O \\
| \\
R
\end{array}
\right]_n
$$

wherein each R is independently selected from H, C_1-C_8 alkyl, C_1-C_8 alkenyl, C_6-C_{10} aryl and C_1-C_8 alkoxy.

14. The deposition composition of claim 11, wherein the precursor comprises a siloxane.

15. The deposition composition of claim 14, wherein the siloxane has the formula

$-(-Si(R)(R)-O-)_n-$

wherein each R is independently selected from H, C_1-C_8 alkyl, C_1-C_8 alkenyl, C_6-C_{10} aryl and C_1-C_8 alkoxy.

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16. The deposition composition of claim 10, wherein the precursor comprises a cube monomer having epoxy and hexyl groups attached to a same cluster of the monomer.

17. The deposition composition of claim 1, wherein said precursor comprises a precursor for forming a high k material on the substrate at deposition temperature below 300°C.

18. The deposition composition of claim 17, wherein the precursor includes a metal selected from the group consisting of Ba, Sr, La, Ti, Zr, Ta and Pb.

19. The deposition composition of claim 17, wherein the precursor includes an organo moiety selected from the group consisting of C_1-C_8 alkoxides, β-diketonates, carbonates, hydroxides, acetates, formates, nitrates, halides, C_6-C_{10} aryls, C_1-C_8 alkyls, and mixtures of two or more of the foregoing.

20. The deposition composition of claim 1, wherein the precursor comprises an organometallic compound selected from the group consisting of tetraphenyl lead and triphenyl bismuth.

21. The deposition composition of claim 1, comprising a solvent/co-solvent species selected from the group consisting of carbon dioxide, water, ammonia and alcohols.

22. The deposition composition of claim 1, wherein the supercritical fluid comprises ammonia.

23. The deposition composition of claim 22, wherein the precursor comprises a precursor for forming a nitride material on the substrate.

24. The deposition composition of claim 23, wherein the precursor has a decomposition temperature below 200°C.

25. The deposition composition of claim 24, wherein the precursor comprises a non-oxide metal-containing precursor.

26. The deposition composition of claim 1, wherein the supercritical fluid comprises carbon dioxide and the precursor comprises a precursor for forming a metal nitride material on the substrate.

27. The deposition composition of claim 1, wherein the precursor comprises a precursor for forming

a copper diffusion barrier material on the substrate.

28. The deposition composition of claim 27, wherein the copper diffusion barrier material comprises a material selected from the group consisting of tantalum (Ta), tantalum nitride (TaN_x), tantalum silicon nitride (TaSiN), titanium nitride (TiN_x), titanium silicon nitride (TiSiN), tungsten nitride (WN_x) and molybdenum nitride (MoN_x), wherein x is equal to the valency of the metal species in the nitride compound.

29. The deposition composition of claim 27, wherein the copper diffusion barrier material comprises an amorphous material.

30. The deposition composition of claim 28, wherein the copper diffusion barrier material comprises an amorphous material.

31. The deposition composition of claim 28, wherein the copper diffusion barrier material comprises a material selected from the group consisting of (TaN_x) and titanium nitride (TiN_x).

32. The deposition composition of claim 28, wherein the copper diffusion barrier material comprises TaSiN.

33. The deposition composition of claim 28, wherein the copper diffusion barrier material comprises a material selected from the group consisting of tungsten nitride (WN_x) and molybdenum nitride (MoN_x).

34. The deposition composition of claim 1, wherein the material comprises a barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal β-diketonates, metal alkoxides, metal alkylamides and metal carbonyls.

35. The deposition composition of claim 1, wherein the material comprises a barrier layer material and the precursor comprises at least one precursor selected from the group consisting of tantalum (V) tetraethoxyacetylacetonate; tantalum (V) (tetraethoxy); tris(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium (III); tantalum (V) ethoxide; tantalum (V) methoxide; tantalum (V) trifluoroethoxide; titanium (IV) n-butoxide; titanium (IV) t-butoxide; titanium (IV) ethoxide; titanium (IV) i-propoxide; pentakis(dimethylamino) tantalum (V); pentakis(ethyl-methylamino)

tantalum (V); tetrakis(diethylamino) titanium; tetrakis(dimethylamino) titanium; Mo(CO)$_6$ and W(CO)$_6$.

36. The deposition composition of claim 1, wherein the material comprises an oxynitride barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal β-diketonates and metal alkoxides.

37. The deposition composition of claim 1, wherein the material comprises a nitride barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal alkylamides.

38. The deposition composition of claim 1, wherein the material comprises a silicide barrier layer material and the precursor comprises at least one silicon-containing precursor.

39. The deposition composition of claim 38, wherein the at least one silicon-containing precursor comprises a precursor species selected from the group consisting of silane and t-butyl silane.

40. The deposition composition of claim 1, wherein the material comprises a copper diffusion barrier layer material and the precursor comprises at least one copper precursor selected from the group consisting of copper (II) β-diketonates, copper (II) carboxylates, copper (I) cyclopentadienes, copper (I) phenyls, copper (I) amides, and Lewis base adducts of the aforementioned copper (I) species.

41. The deposition composition of claim 1, wherein the precursor comprises a metal complex including at least one ligand selected from the group consisting of β-diketonates, carboxylates, cyclopentadiene, phenyls, and amides.

42. The deposition composition of claim 41, wherein the metal complex is fluorine-free.

43. The deposition composition of claim 1, wherein the precursor comprises at least one copper precursor selected from the group consisting of

(1) Cu(acac)$_2$

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(2) Cu(thd)$_2$

(3) Cu(dmhd)$_2$

(4) Cu(bzac)$_2$

(5) Cu(CHB)$_2$

(6) Cu(oxalate)

(7) Cu(formate)$_2$

(8) Cu(acetate)$_2$

(9) (VTMS)Cu(hfac)

(10) Cu(tod)$_2$

(11) CpCuPMe$_3$

(12) Cu(dibm)$_2$

(13) (CO)CuCl

(14) Cu(hfac)$_2$•H$_2$O

(15) Cu(hfac)$_2$

(16) Cu(tfbzm)$_2$

(17) (MHY)Cu(hfac)

(18) (COD)Cu(hfac)

(19) (DMCOD)Cu(hfac)

(20) Cu(pentafluorophenyl) pentamer

(21) (VCH)Cu(hfac)

wherein:

acac = pentane-2,4-dionate

bzac = 1-phenylpentane-1,3-dionate

COD = cyclooctadiene

dibm = 2,6-dimethylheptane-3,5-dionate

dmhd = 1,1-dimethylhexane-3,5-dionate

MHY = 2-methyl-1-hexene-3-yne

tfbzm = 1,1,1-trifluoro-4-phenylbutane-2,4-dionate

thd = 2,2,6,6-tetramethylheptane-3,5-dionate

tod = 2,2,7-trimethyloctane-3,5-dionate

VCH = vinylcyclohexane

CHB = cyclohexanebutyrate

VTMS = vinyltrimethylsilane.

44. The deposition composition of claim 1, wherein the precursor comprises a copper (III) precursor, and the composition further comprises isopropyl alcohol.

45. The deposition composition of claim 1, wherein the material to be formed on the substrate comprises a noble metal and/or a noble metal oxide.

46. The deposition composition of claim 45, wherein the noble metal and/or noble metal oxide comprises a metal/metal oxide species selected from the group consisting of platinum (Pt), iridium (Ir), iridium oxide (IrO_2), ruthenium (Ru), ruthenium oxide (RuO_2), palladium (Pd), silver (Ag), and gold (Au).

47. The deposition composition of claim 45, wherein the precursor comprises a metal precursor selected from the group consisting of

> (i) metal carbonyls;

> (ii) metal (β-diketonate)$_x$•L wherein x = 1, 2 or 3 and L = Lewis base ligand; and

> (iii) mixed ligand compounds.

48. The deposition composition of claim 47, wherein the precursor comprises a metal carbonyl selected from the group consisting of $Ir_3(CO)_{12}$ and $Ru_3(CO)_{12}$.

49. The deposition composition of claim 48, wherein the supercritical fluid comprises supercritical carbon dioxide.

50. The deposition composition of claim 47, wherein the precursor comprises a metal (β-diketonate)$_x$•L wherein x = 1, 2 or 3 and L = Lewis base ligand, selected from the group consisting of

> (1,5-cyclooctadiene)Ir(I)(acac);

> tris(norbornadiene)Ir(III)(acac);

> (vinyltriethylsilane)Ag(I)(hexafluoroacetylacetonato); and

> bis(2,2,6,6-tetramethyl-3,5-heptanedionato)Ru(II)(1,5-cyclooctadiene).

51. The deposition composition of claim 47, wherein the precursor comprises a mixed ligand composition including a compound selected from the group consisting of

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(CH$_3$)$_2$Au(III)(acac);

tetrakis-(triphenylphosphine)platinum (0);

trimethyl-methylcyclopentadienyl platinum (IV); and

tricarbonyl-methylcyclopentadienyl platinum (I).

52. A method of forming a material on a substrate, comprising depositing the material on the substrate from a deposition composition comprising a precursor of said material, and a supercritical fluid.

53. The method of claim 52, wherein the supercritical fluid comprises a fluid selected from the group consisting of: carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, ethane, methanol, ethanol, isopropanol, dimethyl ketone, sulfur hexafluoride, carbon monoxide, dinitrogen oxide, forming gas, hydrogen, and mixtures thereof.

54. The method of claim 52, wherein the supercritical fluid comprises carbon dioxide.

55. The method of claim 52, wherein said composition comprises a co-solvent.

56. The method of claim 52, wherein the deposition composition consists essentially of said supercritical fluid and said precursor.

57. The method of claim 52, wherein the deposition composition consists of said supercritical fluid and said precursor.

58. The method of claim 52, wherein said precursor comprises a barrier layer precursor for forming a metal nitride or metal oxynitride barrier layer.

59. The method of claim 58, wherein said metal nitride or metal oxynitride comprises at least one metal selected from the group consisting of tantalum, titanium, silicon, tungsten and molybdenum.

60. The method of claim 52, wherein said precursor comprises a precursor for forming a mesoporous

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organo-functionalized silsequioxane (SSQ) material on the substrate.

61. The method of claim 52, wherein said precursor comprises a precursor for forming a low k organosilicate material on the substrate.

62. The method of claim 61, wherein the precursor comprises a silsequioxane or siloxane precursor.

5   63. The method of claim 62, wherein the precursor comprises a silsequioxane.

64. The method of claim 63, wherein the silsequioxane has the formula:
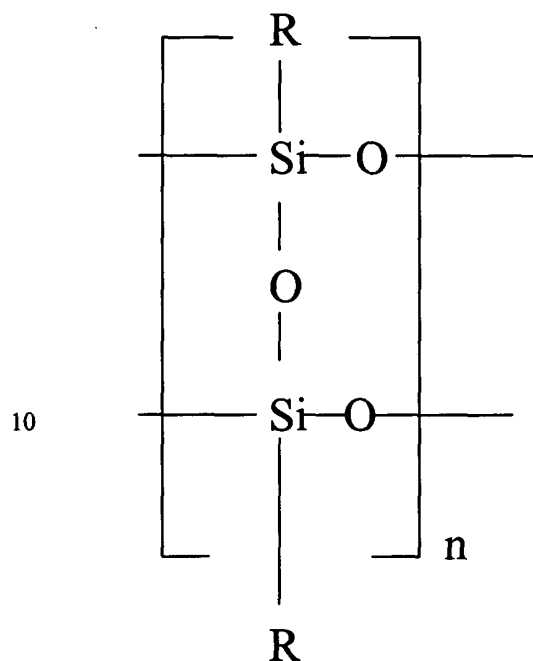
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$$
\left[\begin{array}{c} R \\ | \\ Si{-}O \\ | \\ O \\ | \\ Si{-}O \\ | \\ R \end{array} \right]_n
$$

wherein each R is independently selected from H, C_1-C_8 alkyl, C_1-C_8 alkenyl, C_6-C_{10} aryl and C_1-C_8 alkoxy.

15   65. The method of claim 61, wherein the precursor comprises a siloxane.

66. The method of claim 65, wherein the siloxane has the formula

-(-Si(R)(R)-O-)$_n$-

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wherein each R is independently selected from H, C_1-C_8 alkyl, C_1-C_8 alkenyl, C_6-C_{10} aryl and C_1-C_8 alkoxy.

67. The method of claim 61, wherein the precursor comprises a cube monomer having epoxy and hexyl groups attached to a same cluster of the monomer.

68. The method of claim 52, wherein said precursor comprises a precursor for forming a high k material on the substrate at deposition temperature below 300°C.

69. The method of claim 68, wherein the precursor includes a metal selected from the group consisting of Ba, Sr, La, Ti, Zr, Ta and Pb.

70. The method of claim 68, wherein the precursor includes an organo moiety selected from the group consisting of C_1-C_8 alkoxides, β-diketonates, carbonates, hydroxides, acetates, formates, nitrates, halides, C_6-C_{10} aryls, C_1-C_8 alkyls, and mixtures of two or more of the foregoing.

71. The method of claim 52, wherein the precursor comprises an organometallic compound selected from the group consisting of tetraphenyl lead and triphenyl bismuth.

72. The method of claim 52, comprising a solvent/co-solvent species selected from the group consisting of carbon dioxide, water, ammonia and alcohols.

73. The method of claim 52, wherein the supercritical fluid comprises ammonia.

74. The method of claim 52, wherein the precursor comprises a precursor for forming a nitride material on the substrate.

75. The method of claim 74, wherein the precursor has a decomposition temperature below 200°C.

76. The method of claim 75, wherein the precursor comprises a non-oxide metal-containing precursor.

77. The method of claim 52, wherein the supercritical fluid comprises carbon dioxide and the precursor comprises a precursor for forming a metal nitride material on the substrate.

78. The method of claim 52, wherein the precursor comprises a precursor for forming a copper diffusion barrier material on the substrate.

79. The method of claim 78, wherein the copper diffusion barrier material comprises a material selected from the group consisting of tantalum (Ta), tantalum nitride (TaN_x), tantalum silicon nitride (TaSiN), titanium nitride (TiN_x), titanium silicon nitride (TiSiN), tungsten nitride (WN_x) and molybdenum nitride (MoN_x), wherein x is equal to the valency of the metal species in the nitride compound.

80. The method of claim 78, wherein the copper diffusion barrier material comprises an amorphous material.

81. The method of claim 79, wherein the copper diffusion barrier material comprises an amorphous material.

82. The method of claim 79, wherein the copper diffusion barrier material comprises a material selected from the group consisting of (TaN_x) and titanium nitride (TiN_x).

83. The method of claim 79, wherein the copper diffusion barrier material comprises TaSiN.

84. The method of claim 79, wherein the copper diffusion barrier material comprises a material selected from the group consisting of tungsten nitride (WN_x) and molybdenum nitride (MoN_x).

85. The method of claim 52, wherein the material comprises a barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal β-diketonates, metal alkoxides, metal alkylamides and metal carbonyls.

86. The method of claim 52, wherein the material comprises a barrier layer material and the precursor comprises at least one precursor selected from the group consisting of tantalum (V) tetraethoxyacetylacetonate; tantalum (V) (tetraethoxy); tris(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium (III); tantalum (V) ethoxide; tantalum (V) methoxide; tantalum (V) trifluoroethoxide; titanium (IV) n-butoxide; titanium (IV) t-butoxide; titanium (IV) ethoxide; titanium (IV) i-propoxide; pentakis(dimethylamino) tantalum (V); pentakis(ethyl-methylamino) tantalum (V); tetrakis(diethylamino) titanium; tetrakis(dimethylamino) titanium; $Mo(CO)_6$ and

$W(CO)_6$.

87. The method of claim 52, wherein the material comprises an oxynitride barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal β-diketonates and metal alkoxides.

5   88. The method of claim 52, wherein the material comprises a nitride barrier layer material and the precursor comprises at least one precursor selected from the group consisting of metal alkylamides.

89. The method of claim 52, wherein the material comprises a silicide barrier layer material and the precursor comprises at least one silicon-containing precursor.

10   90. The method of claim 89, wherein the at least one silicon-containing precursor comprises a precursor species selected from the group consisting of silane and t-butyl silane.

91. The method of claim 52, wherein the material comprises a copper diffusion barrier layer material and the precursor comprises at least one copper precursor selected from the group consisting of copper (II) β-diketonates, copper (II) carboxylates, copper (I) cyclopentadienes, copper (I)

15   phenyls, copper (I) amides, and Lewis base adducts of the aforementioned copper (I) species.

92. The method of claim 52, wherein the precursor comprises a metal complex including at least one ligand selected from the group consisting of β-diketonates, carboxylates, cyclopentadiene, phenyls, and amides.

93. The method of claim 92, wherein the metal complex is fluorine-free.

20   94. The method of claim 52, wherein the precursor comprises at least one copper precursor selected from the group consisting of

(1) $Cu(acac)_2$

(2) $Cu(thd)_2$

(3) $Cu(dmhd)_2$

(4) Cu(bzac)$_2$

(5) Cu(CHB)$_2$

(6) Cu(oxalate)

(7) Cu(formate)$_2$

(8) Cu(acetate)$_2$

(9) (VTMS)Cu(hfac)

(10) Cu(tod)$_2$

(11) CpCuPMe$_3$

(12) Cu(dibm)$_2$

(13) (CO)CuCl

(14) Cu(hfac)$_2$•H$_2$O

(15) Cu(hfac)$_2$

(16) Cu(tfbzm)$_2$

(17) (MHY)Cu(hfac)

(18) (COD)Cu(hfac)

(19) (DMCOD)Cu(hfac)

(20) Cu(pentafluorophenyl) pentamer

(21) (VCH)Cu(hfac)

wherein:

acac = pentane-2,4-dionate

bzac = 1-phenylpentane-1,3-dionate

COD = cyclooctadiene

dibm = 2,6-dimethylheptane-3,5-dionate

dmhd = 1,1-dimethylhexane-3,5-dionate

MHY = 2-methyl-1-hexene-3-yne

tfbzm = 1,1,1-trifluoro-4-phenylbutane-2,4-dionate

thd = 2,2,6,6-tetramethylheptane-3,5-dionate

tod = 2,2,7-trimethyloctane-3,5-dionate

VCH = vinylcyclohexane

CHB = cyclohexanebutyrate

VTMS = vinyltrimethylsilane.

95. The method of claim 52, wherein the precursor comprises a copper (III) precursor, and the composition further comprises isopropyl alcohol.

96. The method of claim 52, wherein the material to be formed on the substrate comprises a noble metal and/or a noble metal oxide.

97. The method of claim 96, wherein the noble metal and/or noble metal oxide comprises a metal/metal oxide species selected from the group consisting of platinum (Pt), iridium (Ir), iridium oxide (IrO$_2$), ruthenium (Ru), ruthenium oxide (RuO$_2$), palladium (Pd), silver (Ag), and

gold (Au).

98. The method of claim 97, wherein the precursor comprises a metal precursor selected from the group consisting of

(i) metal carbonyls;

(ii) metal (β-diketonate)$_x$•L wherein x = 1, 2 or 3 and L = Lewis base ligand; and

(iii) mixed ligand compounds.

99. The method of claim 98, wherein the precursor comprises a metal carbonyl selected from the group consisting of $Ir_3(CO)_{12}$ and $Ru_3(CO)_{12}$.

100. The method of claim 99, wherein the supercritical fluid comprises supercritical carbon dioxide.

101. The method of claim 98, wherein the precursor comprises a metal (β-diketonate)$_x$•L wherein x = 1, 2 or 3 and L = Lewis base ligand, selected from the group consisting of

(1,5-cyclooctadiene)Ir(I)(acac);

tris(norbornadiene)Ir(III)(acac);

(vinyltriethylsilane)Ag(I)(hexafluoroacetylacetonato); and

bis(2,2,6,6-tetramethyl-3,5-heptanedionato)Ru(II)(1,5-cyclooctadiene).

102. The method of claim 98, wherein the precursor comprises a mixed ligand composition including a compound selected from the group consisting of

$(CH_3)_2Au(III)(acac)$;

tetrakis-(triphenylphosphine)platinum (0);

trimethyl-methylcyclopentadienyl platinum (IV); and

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tricarbonyl-methylcyclopentadienyl platinum (I).

103. A method of forming a low k organosilicate film on a substrate, comprising contacting the substrate with a deposition composition comprising an organosilicon compound and a supercritical fluid,to deposit a silicon-containing material on the substrate, and vitrifying the silicon-containing material to form said low k organosilicate film as a porous organosilicate film on the substrate.

104. The method of claim 103, comprising controlling the porosity of the porous organosilicate film to yield the porous organosilicate film as a film having a predetermined dielectric constant.

105. The method of claim 104, wherein porosity is controlled by controlled incorporation of air bubbles in the silicon-containing material deposited on the substrate.

106. A method of forming a barrier layer on a substrate, comprising contacting the substrate in a contacting zone with a deposition composition comprising a barrier layer precursor and a supercritical fluid, and continuing said contacting while flowing the deposition composition into the contacting zone, and discharging contacted deposition composition from said contacting zone, to effect growth of the barrier layer to a predetermined thickness.

107. A method of metallizing a semiconductor substrate comprising contacting the substrate with a copper metallization precursor in a supercritical fluid, to deposit copper on the substrate.

108. A method of forming electrodes on a semiconductor substrate comprising contacting the substrate with an electrode material precursor in a supercritical fluid, to deposit electrode material on the substrate.